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## Effects of Abrasive Morphology and Surfactant Concentration on Polishing Rate of Ceria Slurry

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To reveal the mechanism behind the high oxide-to-nitride removal selectivity of ceria slurry in shallow trench isolation (STI) chemical mechanical polishing (CMP), we examined the effects of the abrasive morphology and the concentration of surfactant added to control the selectivity. A slurry with small abrasives showed a more drastic drop in the oxide removal rate as the surfactant concentration increased, compared to a slurry with large abrasives. For the nitride removal rate, however, both slurries showed the same trend. These results can be qualitatively explained from the movement of abrasives through the layer of surfactant adsorbed on the film surface. [DOI: 10.1143/JJAP.42.1150]

KEYWORDS: CMP, slurry, ceria, abrasive, surfactant, selectivity, oxide, nitride, zeta potential

### 1. Introduction

Chemical mechanical polishing (CMP) is essential in contemporary ULSI fabrication. The shallow trench isolation (STI) process is one of the most important applications of CMP and has replaced the local oxidation of silicon (LOCOS) method because of its superiority for planarizing the base surface in a multi-layer wiring process. In current-generation STI planarization, the residual thicknesses of the gap-filling oxide and mask nitride layers after CMP must be controlled to within a few tens of nanometers. For slurry used in STI CMP, the removal selectivity between oxide and nitride films is a critical factor because it can determine the STI process margin, and ultimately, the product yield. Compared with the silica slurry that is widely used in oxide polishing, ceria slurry offers greater oxide-to-nitride selectivity in the polishing removal rate. One way to increase the oxide-to-nitride selectivity is to add surfactant to ceria slurry.<sup>1–4)</sup> In addition, controlling the abrasive morphology is essential to improving slurry performance. Although Homma *et al.* reported the dependence of the thermal oxide removal rate on crystallite size,<sup>5)</sup> as far as we know the complex effects of the abrasive morphology and surfactant concentration have not been reported.

In this study, we have investigated how the abrasive morphology and the concentration of surfactant added to ceria slurry affect the oxide and nitride removal rates. To interpret our results, we propose a qualitative model based on the movement of abrasives through the layer of the surfactant adsorbed on the film surface.

### 2. Experimental

We prepared conventional 8'' silicon wafers for this study. Oxide films were deposited using the plasma-enhanced tetraethyl-ortho-silicate (PETEOS) method. Nitride films were formed by low-pressure chemical-vapor deposition (LPCVD). The thicknesses of the as-deposited oxide and nitride films were 7000 and 1500 Å, respectively. The films were polished on a Strasbaugh 6EC with a single polishing head and a polishing platen. We used an IC1000/Suba IV stacked pad (Rodel Co.). The polishing pressure, applied as a down force, was 4 psi (pounds per square inch) and the backpressure was 0 psi. The rotation speed of both the head

and the table was 70 rpm, and the relative velocity between the pad and the wafer was 250 fpm (feet per minute). The slurry flow rate was 100 cm<sup>3</sup>/min and the polishing time was 30 s. Before each polishing, *ex-situ* conditioning was done with a diamond dresser. The film thicknesses before and after CMP were measured with a Nanospec 180 (Nanospecs).

Two kinds of ceria slurry, denoted as A and B, were prepared for this study. The solid-state displacement reaction method and the wet chemical precipitation method were employed with cerium carbonate and cerium nitrate as the starting materials for A and B, respectively. To examine the improvement in the oxide-to-nitride selectivity of these slurries, an anionic organic surfactant (water-soluble acrylic acid) was added with the concentration from 0 to 0.8 wt%. The slurries were then diluted with deionized water so that the solid loading of the ceria abrasives was 1 wt%.

The zeta potential and particle sizes of the abrasives were measured with an AcoustoSizer II (Colloidal Dynamics).<sup>6)</sup> High-resolution photographs of the abrasives were taken with a transmission electron microscope (TEM; JEOL JEM-2010). The number of scratches on the oxide film surface was counted using a Surfscan SP1 (KLA-Tencor). The minimum detecting size of light point defects (LPDs) was adjusted to 0.189 µm.

### 3. Results and Discussion

Figures 1 and 2 show bright-field and dark-field images, respectively, of the abrasives in each slurry. The images were taken by high-resolution TEM. From Fig. 1, it is seen that slurry B was almost composed of discrete single-crystal particles, while slurry A was composed of poly-crystalline abrasives with grain sizes larger than 100 nm. These results are confirmed by Fig. 2, which shows that the particles in slurry B had random crystal orientations, while those in slurry A had small-angle grain boundaries. Note that the orientation differences among grains can be estimated from the differences in image contrast in the dark-field image. The size distributions of the single-crystal grains and the abrasives as poly-crystal particles for slurries A and B are shown in Fig. 3, which were analyzed after the TEM photos. The average size of the single-crystal grains composing the abrasive is similar for slurries A (38.5 nm) and B (40.3 nm), but the average size of the poly-crystal abrasives for slurry A was 121.8 nm and much larger than that for slurry B

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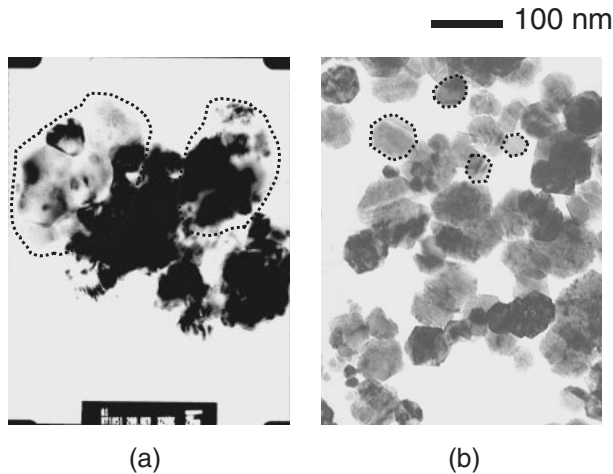


Fig. 1. High-resolution TEM photographs (bright-field image): (a) slurry A, (b) slurry B. Slurry A was composed of poly-crystalline abrasives with sizes larger than 100 nm and slurry B was almost composed of discrete single-crystal particles 30 to 60 nm in size (circled).

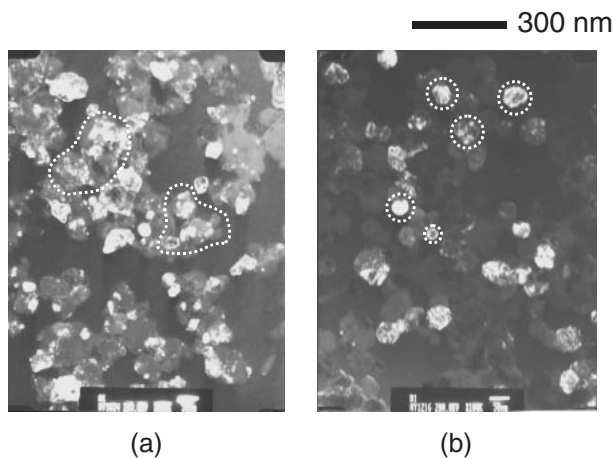


Fig. 2. High-resolution TEM photographs (dark-field image): (a) slurry A, (b) slurry B. The abrasives in slurry A had poly-crystalline structure with small-angle grain boundaries and the abrasives in slurry B had random orientation (circled).

(50.8 nm). This result means that an abrasive particle in slurry A is composed of around 30 single-crystal grains on average, while that in slurry B is composed of one or two grains. In a polishing slurry, the abrasives generally agglomerate and form secondary particles via van der Waals force, however this kind of interaction between abrasives should be weaker than the grain boundary binding force originated in hetero-polar bonds. Based on the discussion above, it is thought that the abrasives in slurry B were easily reduced to smaller particles than those in slurry A by the shear stress during polishing.

Figure 4 shows the oxide film removal rate versus surfactant concentration for slurries A and B. The oxide removal rate of slurry B without surfactant was around half that of slurry A. The rate for slurry B drastically decreased, however, with a small amount ( $\sim 0.08$  wt%) of surfactant added, while the rate for slurry A did not decrease much for surfactant concentrations up to 0.40 wt%.

The nitride film removal rate is plotted versus surfactant concentration in Fig. 5. The ratio of the oxide and nitride

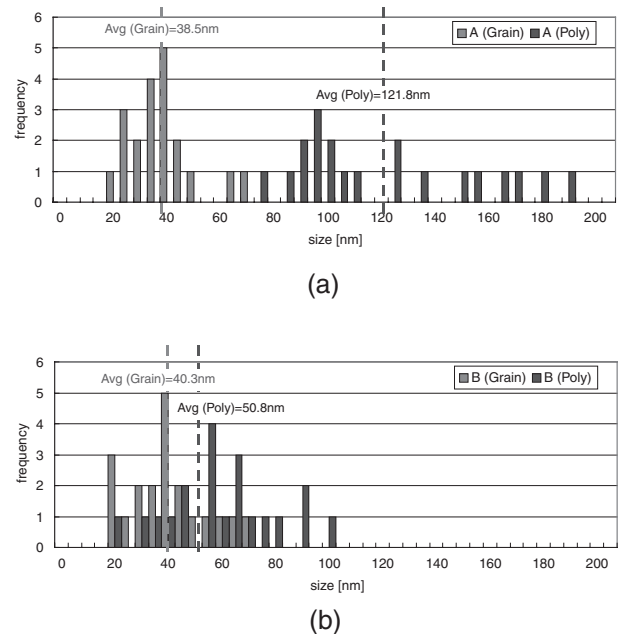


Fig. 3. Size distributions of the single-crystal grains and the abrasives as poly-crystal particles: (a) slurry A, (b) slurry B.

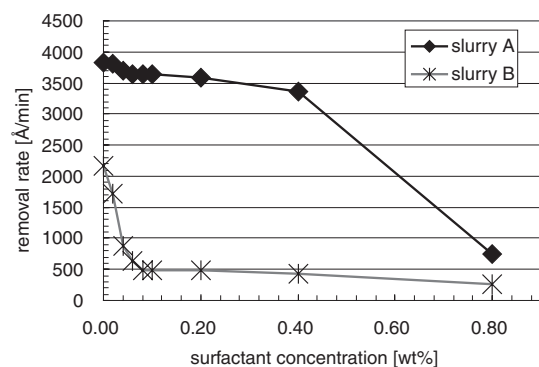


Fig. 4. Oxide film removal rate versus surfactant concentration.

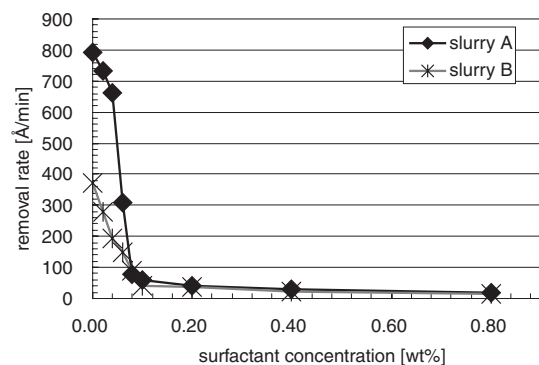


Fig. 5. Nitride film removal rate versus surfactant concentration.

removal rates without surfactant was around 5 : 1 for both slurries, and this value is similar to that for a typical silica slurry. With increasing surfactant concentration, the nitride removal rates for both slurries drastically decreased and were almost saturated at a surfactant concentration of 0.10 wt%.

In Fig. 6, which shows the zeta potential of the particles



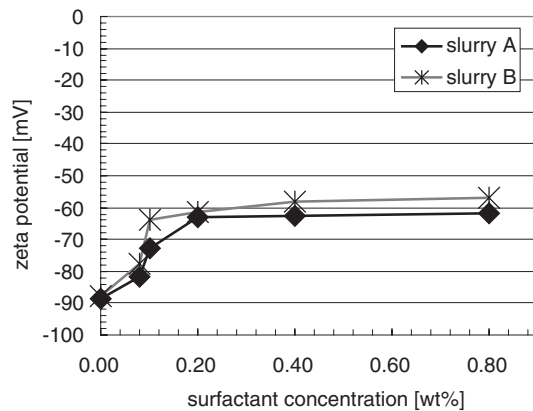


Fig. 6. Zeta potential versus surfactant concentration, measured with the AcoustoSizer.

versus surfactant concentration, there are no large differences in zeta potential between the slurries at any surfactant concentration within our experimental range. Since the zeta potential of the film surface is independent of the particle characteristics, the electrostatic interactions between the particles and the film surface are thought to be almost the same for slurries A and B. Therefore, the differences in removal rates cannot be explained just from the electrostatic interactions, while Tateyama *et al.* pointed out that the surfactant adsorption on ceria abrasives, which determines the zeta potential of abrasives, is dominant phenomenon for planarization using ceria abrasives.<sup>4)</sup>

Hence, it is necessary to understand the abrasive behavior in slurry fluid, especially near the film surface on which the surfactant is adsorbed or segregated. Runnels *et al.* analyzed the fluid layer between the wafer and pad and calculated the thickness of the fluid layer.<sup>7)</sup> Philipossian calculated the Stokes number of the abrasives in slurry and showed that abrasives with a reasonable size (*e.g.*, smaller than 2–3  $\mu\text{m}$ ) flow with the fluid during polishing.<sup>8)</sup> As the fluid is thought to stick to the film surface at the solid-liquid boundary because of its viscosity, let us consider a particle, accelerated by pad movement near the film surface, that travels through the viscous fluid and can approach the film surface. Suppose that the particle can be treated as spherical and the effect of gravity can be ignored. The Reynolds number in the fluid is  $Re = \rho Ur/\mu$ , where  $\rho$  is the fluid density,  $U$  is the velocity of the particle,  $r$  is the radius of the particle, and  $\mu$  is the viscosity.<sup>9)</sup> The slurry density is about 1000 kg/m<sup>3</sup>, the pad velocity (and thus, the particle initial velocity) is approximately 1.25 m/s, and the slurry viscosity is about  $1 \times 10^{-3}$  Pa·s. Assuming a particle radius of 200 nm, this gives  $Re \sim 0.25$ .

This extremely small value for  $Re$  implies that Stokes' law of resistance, namely  $F = 6\pi\mu rU$ , can be applied, where  $F$  is the resistance force against a particle moving in a fluid. Then, the velocity of the particle as a function of time  $t$  can be written with the differential equation  $dU/dt = -6\pi\mu r m^{-1}U$ , where  $m = (4/3)\pi r^3 D$  is the mass of the particle and  $D$  is the density of the particle. This gives

$$U = U_0 \exp\{-(9/2)\mu D^{-1} r^{-2} t\}, \quad (1)$$

where  $U_0$  is the initial velocity. This means that larger particles can approach the film surface more effectively,

with less reduction in their velocities. It can thus be deduced that larger particles are more likely to reach the film surface, through the viscous layer of surfactant adsorbed on the surface. Here, the amount of surfactant adsorption (or segregation on the surface) depends on the bulk concentration of the surfactant and the electrostatic interaction between the surfactant and the film surface. As more surfactant is adsorbed, the viscosity [ $\mu$  in eq. (1)], which describes particle behavior near the surface, should increase and impede the movement of particles. The adsorbed surfactant thus acts as a passivation layer preventing particles from contacting the film surface. In a real case, the electrostatic interaction between the surface and a particle must also be taken into account, but since the measured zeta potentials of slurry A and slurry B have no large difference (as shown in Fig. 6), the discussion above should be qualitatively correct.

Figure 7 shows the average particle size, measured with the AcoustoSizer, versus surfactant concentration. The measured particle size of slurry B was around 130–170 nm and did not show much variation over the whole range of this study. On the other hand, the particle size of slurry A increased from 150 to 300 nm with increasing surfactant concentration. Compared with the results in Fig. 3, the AcoustoSizer measurements show that the abrasives in the slurry were more or less agglomerated and formed secondary particles. During polishing, the abrasives in slurry B are thought to be easily reduced to smaller particles ( $\sim 50$  nm) than those in slurry A as discussed above.

Figure 8 shows the number of scratches on the PETEOS film after CMP using slurry A or B. The surfactant concentration were 0.40 wt% and nine wafers were polished and measured for each slurry. The average number of scratches for slurry A (1.33 counts/wafer) was a little larger than that for slurry B (0.89 counts/wafer). Tateyama *et al.* reported that the number of scratches on a wafer after CMP rapidly increases as the mean secondary particle size gets larger than 340 nm,<sup>4)</sup> so the mean particle size of slurry A might be near the critical value as for avoiding scratches. As for our results, however, the number of scratches for both slurries were much fewer than those reported by Tateyama *et al.*<sup>4)</sup> so it can be said that the uncontrolled large particles (*e.g.*  $>1 \mu\text{m}$ ) were well eliminated.

From the discussion above, a mechanism explaining the

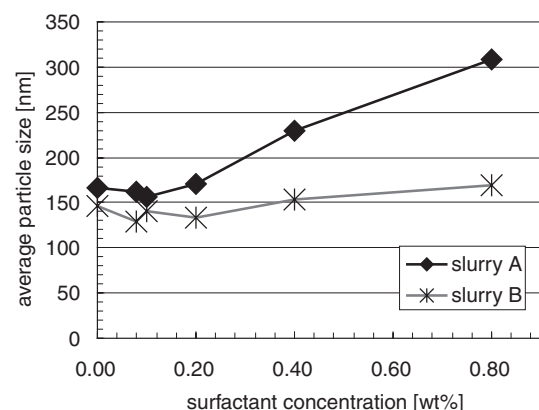


Fig. 7. Average particle size versus surfactant concentration, measured with the AcoustoSizer.

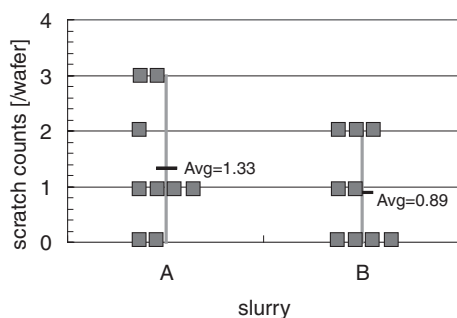


Fig. 8. Number of scratches on PETEOS film after CMP. Nine wafers were polished and measured for each slurry. The result for a wafer is plotted with a square mark.

CMP results shown in Figs. 4 and 5 can be deduced as follows: When the surfactant is not added to the slurry to control the oxide-to-nitride selectivity, both large abrasives (like in slurry A) and small abrasives (like in slurry B) can directly contact the oxide and nitride surfaces and contribute to surface removal.<sup>10)</sup> With increasing surfactant concentration, the amount of surfactant adsorbed on the film surface increases. It then becomes more difficult for small abrasives to approach the surface than large abrasives, which explains the results shown in Fig. 4. On the other hand, the amount of adsorption on a nitride film is larger than that on an oxide film for the same surfactant concentration.<sup>2,11)</sup> Therefore, with even a small surfactant concentration (*e.g.*, 0.10 wt% in this study), large abrasives also have difficulty reaching the film surface and removing it, which explains the results shown in Fig. 5.

#### 4. Conclusion

We have investigated the effects of abrasive morphology and surfactant concentration on film removal by conducting CMP experiments using two kinds of ceria slurry and wafers with blanket film. The slurry with smaller abrasives showed

the more drastic drop in the oxide removal rate as the surfactant concentration increased. For the nitride removal rate, however, both slurries showed the same trend. These results can be qualitatively explained from the movement of abrasives though the layer of surfactant adsorbed on the film surface.

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